PREPARATION AND REDUCTION BEHAVIOR OF CARBON COMPOSITE PELLETS USING SEMI-CHARCOAL[1]

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Abstract

Japanese cypress was carbonized partly at maximum carbonization temperature $T_{C,\ max}$ = 823, 1,073 and 1,273 K in order to obtain semi-charcoal with some residual volatile matter (V.M.). The semi-charcoal obtained at $T_{C,\ max}$ = 823 K retained much V.M., mainly H_2. The gasification of semi-charcoal and coke samples were carried out at gasification temperature T_G = 1,073 K, 1,173 K and 1,273 K in CO_2 gas atmosphere. The gasification rate of a semi-charcoal sample obtained at $T_{C,\ max}$ = 823 K was the highest, but the difference of rate in all semi-charcoal samples were much small. The activation energy was estimated as 138 kJ/mol, 139 kJ/mol, 162 kJ/mol and 219 kJ/mol, respectively for semi-charcoal obtained at $T_{C,\ max}$ = 823 K, 1,073 K, 1,273 K and coke samples. Then, carbon composite pellets using semi-charcoal with the particle size of 63～75 µm have been prepared and reduced at reduction temperature T_R = 1,173 K in N_2 gas atmosphere. Fractional reduction *F*(%) after 60 min of the carbon composite pellet using semi-charcoal obtained at $T_{C,\ max}$ = 823 K was 40%, and was higher than any other pellets. On the other hand, fractional reduction *F*(%) of carbon composite pellet using semi-charcoal obtained at $T_{C,\ max}$ = 1,073 K with the particle size of 23～35 µm was 38% for 60 min at T_R = 1,173 K, and was higher than any other pellets with the particle sizes of 63～75 µm and 105～150 µm.

Key words: Carbon composite pellet; Charcoal; Reduction of iron oxide, Carbonization.

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[1] *Technical contribution to the 6th International Congress on the Science and Technology of Ironmaking – ICSTI, 42nd International Meeting on Ironmaking and 13th International Symposium on Iron Ore, October 14th to 18th, 2012, Rio de Janeiro, RJ, Brazil.*

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1 INTRODUCTION

The Kyoto Protocol came into effect in February 2005, and the first agreement period was to begin from 2008. As declared in the Kyoto Protocol, Japan is targeting a 6% decrease in greenhouse gas (GHG) emissions in 2010 compared with the baseline year 1990. However, Japan's total GHG emissions in 2004 were reported as 7.4% increase in comparison with 1990, up to 1.355 billion tons. In a serious situation, the Japanese steel industry has already targeted a 10.5% decrease in CO_2 emissions of 2010 under a Voluntary Action Plan adopted by the Japan Iron and Steel Federation.[1] A lot of steel engineers researched various means to decrease reducing agents at a blast furnace in order to reduce CO_2 emissions. For example, injection of waste plastics and carbon neutral materials such as biomass into a blast furnace is better alternative.[2,3] Especially, biomass has a novel advantage, i.e., no CO_2 emissions, because of carbon neutral. Recently, charcoal composite iron oxide pellets were proposed to decrease CO_2 emissions for the ironmaking. These pellets were promising to decrease the starting temperature for iron oxide reduction in carbon composite iron ore agglomerates under a rising temperature condition, such as in a blast furnace shaft.

On the other hand, we have already studied the novel iron ore agglomerate using semi-coal-char with some residual volatile matter (V.M.).[4-7] This semi-coal-char with residual V.M. is obtained when the carbonization of coal under a rising temperature condition is interrupted at a certain temperature, i.e., a maximum carbonization temperature, $T_{C,\ max}$. These agglomerates using such semi-coal-char have high reducibility at low temperature and some strength as well. While simple iron ore agglomerate using an usual char will start the reduction reaction as solid-solid reaction at somewhat higher temperature, the proposed one will start the reduction reaction as gas-solid reaction at somewhat lower temperature but a little higher than $T_{C,\ max}$ under a rising temperature condition. Furthermore, in a case of using the semi-charcoal as carbonaceous materials of these agglomerates, the reaction rate of iron oxide reduction could be much higher than that of semi-coal-char at low temperature. Because the reduced gases, H_2 and CO, in the semi-charcoal could be released larger than those of semi-coal-char from same $T_{C,\ max}$ and the reactivity of semi-charcoal on the gasification is much higher at low temperature due to amorphous structure and large specific surface area. So the partial carbonization of biomass at low $T_{C,\ max}$ is important process in order to obtain such semi-charcoal.

From these backgrounds, we propose carbon composite iron oxide pellets using semi-charcoal in order to decrease reducing agents at a blast furnace and CO_2 emissions. In this work, semi-charcoal composite iron oxide pellets have been prepared and the effect of residual V.M. and gasification rate of semi-charcoal on reduction of iron oxide were investigated. Furthermore, the effect of the semi-charcoal particle size was also investigated.

2 EXPERIMENTAL

2.1 Sample

Japanese cypress as woody biomass and reagent grade hematite Fe_2O_3 (95 mass%, Wako Pure Chemical Industries, Ltd.) as an iron oxide sample were used. The analysis value of Japanese cypress and Newcastle blend coal as a comparative sample are shown in Table 1. Japanese cypress has much V.M. of 90.8 mass%. The amount of oxygen in Japanese cypress is 41.1 mass% and is much larger than that of 9.27 mass% in coal. Carbonization of Japanese cypress under a rising temperature condition was interrupted at maximum carbonization temperature, $T_{C,\,max}$ = 823, 1073 and 1273 K, to obtain semi-charcoal with some residual V.M.

Table 1. Analysis value of (a) Japanese cypress and (b) Newcastle blend coal as a comparative sample

(a) Japanese cypress (mass%)

F.C.	V.M.	Ash	C	H	O	N	S
8.12	90.8	1.05	50.7	6.16	41.1	1.01	0.014

(b) Newcastle blend coal (mass%)

F.C.	V.M.	Ash	C	H	O	N	S
58.7	32.8	8.52	74.8	4.90	9.27	1.97	0.54

2.2 Preparation of Semi-charcoal

Japanese cypress (200 g) as woody biomass was carbonized partly in order to obtain the semi-charcoal with some residual V.M. A schematic draw of experimental apparatus is shown in Figure 1. Chips of the wood were packed in the carbonization reactor. N_2 gas was entered from the top of the reactor, which was then heated at 200 K h^{-1} by a digital thermo-controller. Beforehand, N_2 gas with a constant flow rate of 1.67×10^{-5} (m^3 s^{-1} (s.t.p.)) was passed through the packed bed and mixed with the carbonizing gas to determine each gas flow rate. This outlet gas mixture was filtered through glass wool to remove the tar. The resultant gas was cooled by ice and water to condense the water vapor. After the water vapor was captured in the condenser, the carbonizing gas without tar was analyzed by the gas chromatograph (GC14B, Shimadzu Corporation).

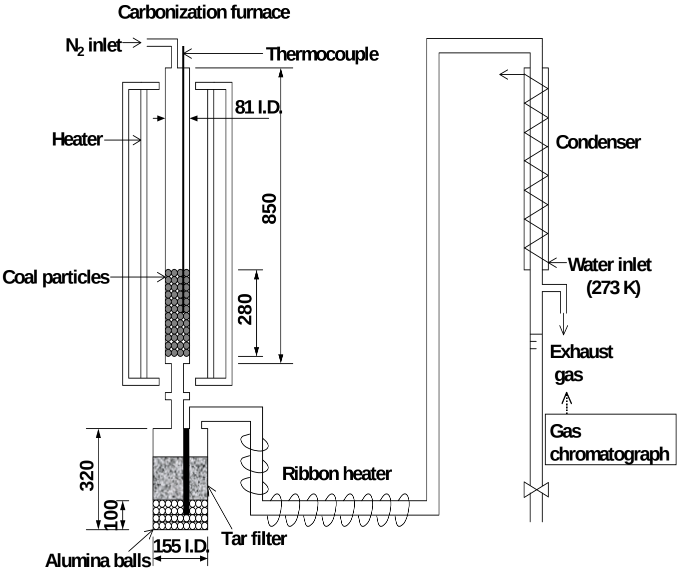

Figure 1. A schematic view of experimental apparatus for carbonization; dimensions in mm.

2.3 Gasification Experiment

The semi-charcoals obtained by carbonization at $T_{C,\ max}$ = 823, 1073 and 1273 K were regulated as 63～75 µm by the sieves. Then, a binder of 1 mass% was added to the semi-charcoal in order to strengthen. The semi-charcoal sample was prepared by handrolling. The size of semi-charcoal and coke sample as a comparative sample was about 12 mm in diameter. These samples were kept at 378 K for 24 h in the dry oven in order to remove water. Then, these samples were heated from room temperature to gasification temperature T_G = 1073, 1173 and 1273 K in N_2 gas atmosphere. The gadsification of semi-charcoal and coke samples were carried out in CO_2 gas atmosphere. Gasification rate was calculated fom the weight loss change of semi-charcoal and coke samples.

2.4 Reduction Experiment

The obtained semi-charcoal was mixed with reagent grade hematite Fe_2O_3 in the mass ratio of one to four. Then, Bentonite of 1 mass% was added to the mixture as a binder in order to strengthen. The semi-charcoal particle size range of the mixture was regulated as 23～63, 63～75 and 105～150 µm by the sieves. The semi-charcoal composite pellet was prepared by handrolling. The size of semi-charcoal composite pellet and coke composite pellet as a comparative sample was 14 and 12 mm in diameter and the density was 4.64×10^5 and 7.37×10^5 g m^{-3}, respectively. These pellets were kept at 378 K for 24 h in the dry oven in order to remove water. Then, these pellets were reduced at reduction temperature T_R = 1173 K in N_2 gas atmosphere in order to investigate the reduction behavior of pellets. The generated gases of H_2, CO, CO_2, CH_4, C_2H_4+C_2H_6+C_3H_8 and H_2O were analyzed by gas chromatography and quadrupole mass spectrometry. Fractional reduction *F*(%) was calculated by equation (1).

$$F(\%) = 100 \times \frac{M_{\mathrm{O\ in\ reaction\ gas}} - M_{\mathrm{O\ in\ volatile\ matter}}}{R_{\mathrm{O}}} \qquad (1)$$

$M_{\mathrm{O\ in\ reaction\ gas}}$ is total molar of oxygen in generated gases on the iron oxide reduction. $M_{\mathrm{O\ in\ volatile\ matter}}$ is total molar of oxygen in the released gas on carbonization of carbonaceous materials. R_{O} is total molar of oxygen in a case of reducing Fe_2O_3 as an iron oxide sample perfectly.

3 RESULTS AND DISCUSSION

3.1 Carbonization of Japanese Cypress

In order to obtain the semi-charcoal with some residual V.M., Japanese cypress was carbonized from room temperature to maximum carbonization temperature $T_{C,\ max}$ = 823, 1073 and 1273 K at 200 K h^{-1}, and kept at $T_{C,\ max}$ until arrival time of 6 h in every case. The obtained variations of main gas flow rates with carbonization time are shown in Figures 2-4. Figure 2 shows the variation of gas flow rates with carbonization time from room temperature to $T_{C,\ max}$ = 823 K. Releasing of CO and CO_2 gases start from carbonization temperature T_C = 573 K, and the flow rates reach the maximum point at T_C = 673 K. CH_4 gas starts from T_C = 673 K, but the flow rate is much lower than those of CO and $CO_{2.}$ Then, H_4 and C_2H_4+C_2H_6+C_3H_8 gases are hardly released from room temperature to $T_{C,\ max}$ = 823 K. Figure 3 shows the variation of gas flow rates with carbonization time from room temperature to $T_{C,\ max}$ = 1073 K. CO and CO_2 gases flow rates gradually decrease over the maximum point at T_C = 673 K. CH_4 gas flow rate reaches the maximum point at T_C = 873 K. H_2 gas is released from carbonization temperature T_C = 873K, and the flow rate reaches the maximum point at $T_{C,\ max}$ = 1073 K. Small amount of C_2H_4+ C_2H_6+ C_3H_8 gases are released from T_C = 673 K to T_C = 873 K. Figure 4 shows the variation of gas flow rates with carbonization time from room temperature to $T_{C,\ max}$ = 1273 K. CO, CO_2, CH_4 and C_2H_4+ C_2H_6+ C_3H_8 gases are hardly released over 1173 K. H_2 gas flow rate gradually decreases from T_C = 1073 K to $T_{C,\ max}$ = 1273 K. But H_2 gas is released partially at $T_{C,\ max}$ = 1273 K. Total gas volumes generated by carbonization are calculated by integrating these gases flow rates, and are shown in Figure 5. H_2 gas volume is larger than any other gases volumes at $T_{C,\ max}$ = 1273 K, but is little at $T_{C,\ max}$ = 823 K. CO and CO_2 gases volumes are larger than any other gases volumes at $T_{C,\ max}$ = 823 K and 1073 K. The volume of CH_4 gas is less than that of CO and CO_2. The volumes of C_2H_4+ C_2H_6+ C_3H_8 gases are little at all contditions. This result was different from results of carbonization of coal. In a case of carbonization of coal, CH_4 gas was released larger than CO and CO_2.[7] This was caused by larger amount of oxygen in Japanese cypress than that in coal. (Table 1)

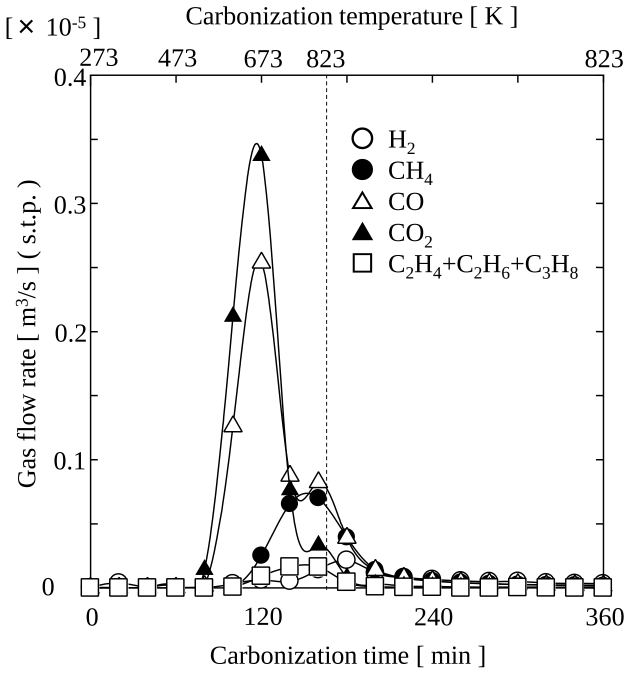

Figure 2. Variation of gas flow rate with carbonization time using Japanese cypress at $T_{C,max}$ = 823 K in N_2 gas atmosphere.

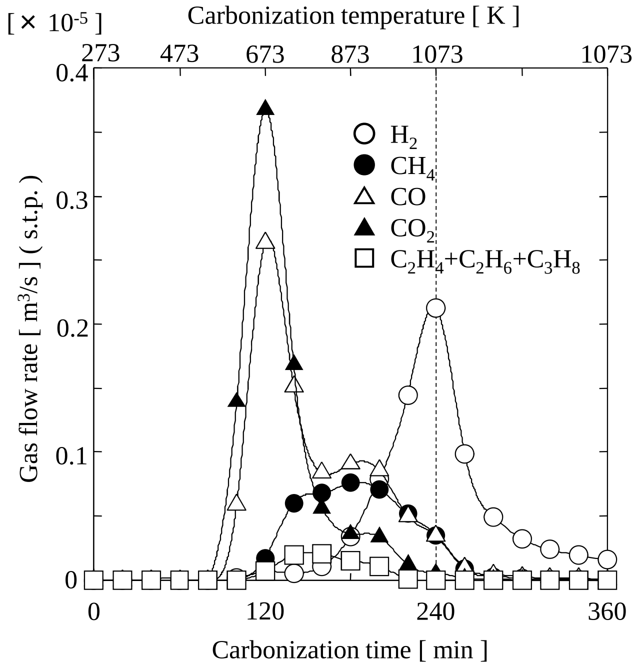

Figure 3. Variation of gas flow rate with carbonization time using Japanese cypress at $T_{C,max}$ = 1073 K in N_2 gas atmosphere.

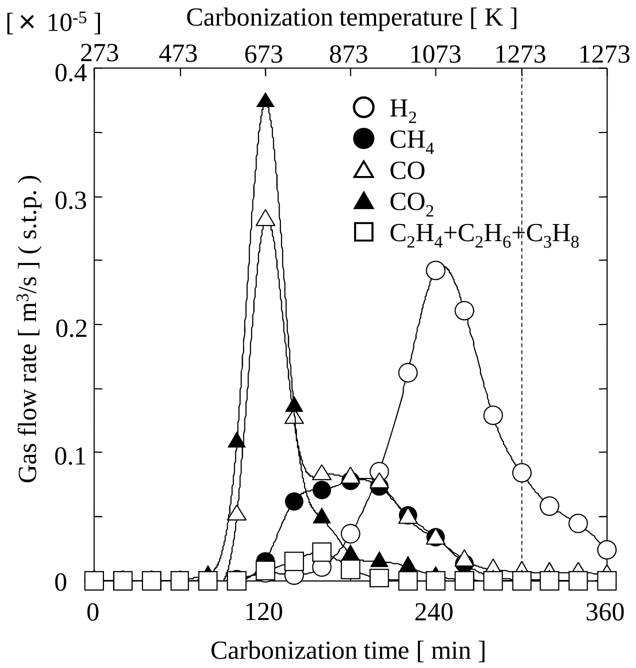

Figure 4. Variation of gas flow rate with carbonization time using Japanese cypress at $T_{C,max}$ = 1273 K in N_2 gas atmosphere.

ISSN 2176-3135

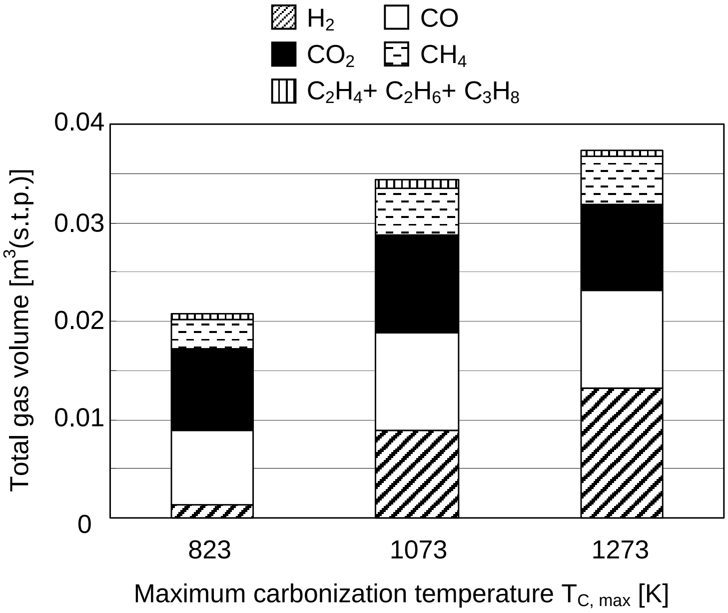

Figure 5. Total gas volume generated by the carbonization of Japanese cypress as a function of $T_{C,\ max}$.

On the other hand, the analysis values of semi-charcoal obtained by carbonization at $T_{C,\ max}$ = 823, 1073 and 1273 K and coke as a comparative sample are shown in Table 2. As $T_{C,\ max}$ went down, the ratios of V.M. and H increased in semi-charcoal. From these results, it was found that the semi-charcoal retained much V.M., mainly H_2, in this case of carbonization at $T_{C,\ max}$ = 823 K and that the semi-charcoal with some residual V.M. could be prepared by controlling $T_{C,\ max}$ in the carbonization.

Table 2. Analysis value of semi-charcoal obtained by carbonization of Japanese cypress at $T_{C,\ max}$ = (a) 823 K, (b) 1073 K (c) 1273 K and coke

(a) $T_{C,\ max}$ = 823 K (mass%)

F.C.	V.M.	Ash	C	H	O	N	S
80.60	18.65	0.76	85.8	2.93	9.89	0.60	0.01

(b) $T_{C,\ max}$ = 1073 K

F.C.	V.M.	Ash	C	H	O	N	S
89.35	9.64	1.01	91.2	1.33	5.89	0.55	0.03

(c) $T_{C,\ max}$ = 1273 K

F.C.	V.M.	Ash	C	H	O	N	S
91.80	7.00	1.16	92.6	0.56	4.81	0.82	0.04

(d) Coke

F.C.	V.M.	Ash	C	H	O	N	S
87.10	0.97	11.97	84.6	0.26	1.35	1.22	0.60

3.2 Gasification of Semi-charcoal

The semi-charcoal samples obtained by carbonization at $T_{C,\ max}$ = 823, 1073 and 1273 K and a coke sample were heated from room temperature to gasification temperature T_G = 1073, 1173 and 1273 K in N_2 gas atmosphere. The gadsification of semi-charcoal and coke samples were carried out in CO_2 gas atmosphere. Figure 6 shows the weight loss curves of the semi-charcoal and coke samples at T_G = 1073 K in CO_2 gas atmosphere. The weight loss change of semi-charcoal sample at $T_{C,\ max}$ = 823 K is the largest. The weight loss change is larger with being lower $T_{C,\ max}$. Then, the weight loss change of coke sample is little. This indicated that the gasification of coke sample didn't start at T_G = 1073 K. Figure 7 shows the weight loss curves of the semi-charcoal and coke samples at T_G = 1173 K in CO_2 gas atmosphere. The weight loss change of semi-charcoal sample at $T_{C,\ max}$ = 823 K is also the largest, but the difference of weight loss in all semi-charcoal samples are much small. Then, the weight loss change of coke sample is much small. Figure 8 shows the weight loss curves of the semi-charcoal and coke samples at T_G = 1273 K in CO_2 gas atmosphere. The weight loss change of semi-charcoal sample at $T_{C,\ max}$ = 823 K is also the largest. The weight loss change of coke sample at T_G = 1273 K is much larger than that at T_G = 1073 and 1173 K. This indicated that the gasification of coke sample was accelerated at T_G = 1273 K.

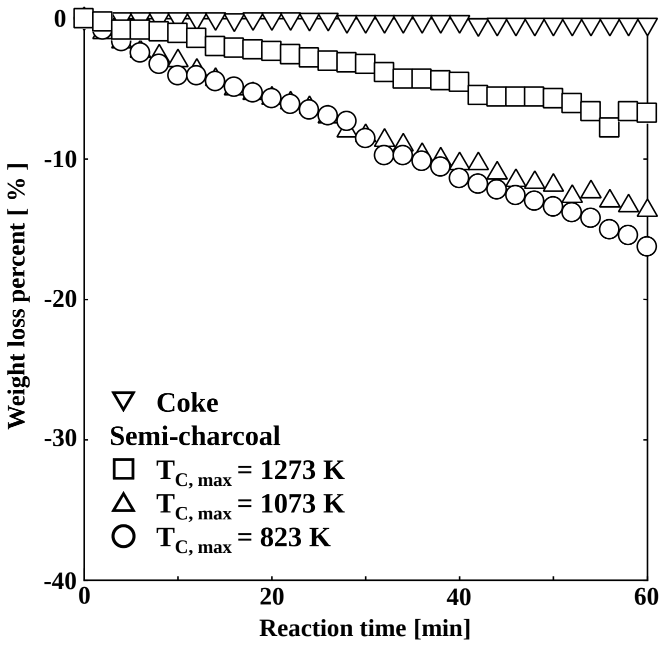

Figure 6. Weight loss curves of semi-charcoal samples obtained by carbonization at $T_{C,\ max}$ = 823, 1073, 1273 K and a coke sample at T_G = 1073 K in CO_2 gas atmosphere.

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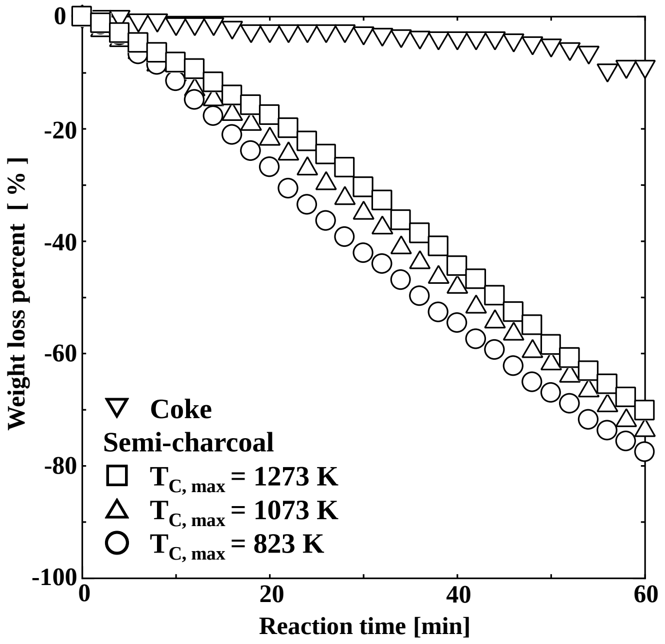

Figure 7. Weight loss curves of semi-charcoal samples obtained by carbonization at $T_{C,\ max}$ = 823, 1073, 1273 K and a coke sample at T_G = 1173 K in CO_2 gas atmosphere.

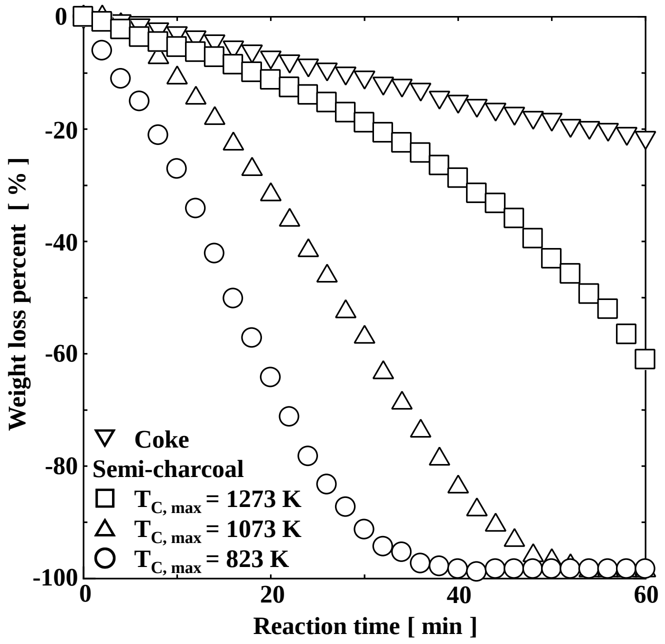

Figure 8. Weight loss curves of semi-charcoal samples obtained by carbonization at $T_{C,\ max}$ = 823, 1073, 1273 K and a coke sample at T_G = 1273 K in CO_2 gas atmosphere.

Gasification rate was calculated fom the weight loss change of semi-charcoal and coke samples. Figure 9 shows the Arrhenius plot of the gasification rate. The gasification rate of a semi-charcoal sample at $T_{C,\ max}$ = 823 K is the highest at all conditions, but the difference of the rates in all semi-charcoal samples are much small. On the other hand, the slope of line with a coke sample is the highest. The slopes of lines with semi-charcoal samples are similar to each other. From the slopes of llines, the activation energy was estimated as 138, 139, 162 and 219 kJ/mol, respectively for semi-charcoal at $T_{C,\ max}$ = 823, 1073, 1273 K and coke samples. This result of activation energy of might be influenced by specific surface area and crystallization of these samples.

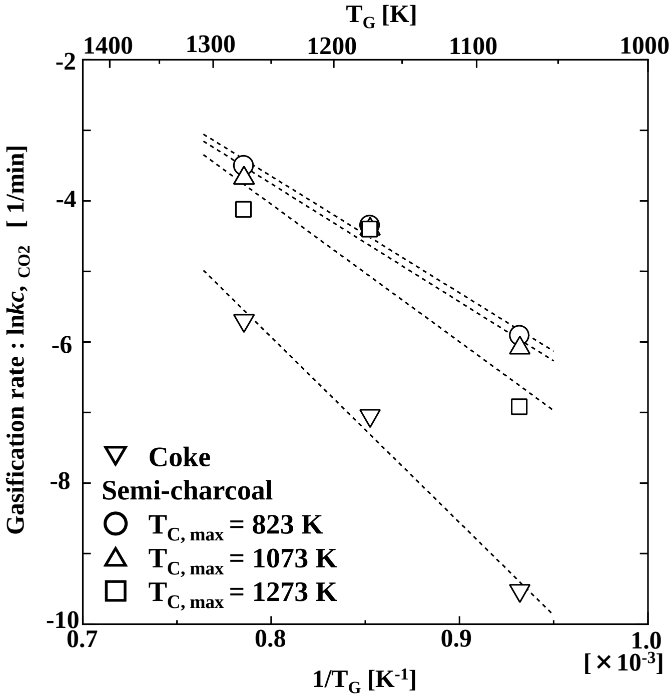

Figure 9. The Arrhenius plot of gasification rate of semi-charcoal samples obtained by carbonization at $T_{C,\ max}$ = 823, 1073, 1273 K and a coke sample at T_G = 1073, 1173, 1273 K in CO_2 atmosphere.

3.3 Reduction Behavior of Semi-charcoal Composite Pellets

In order to investigate the reduction behavior, carbon composite iron oxide pellets using semi-charcoals obtained at $T_{C,\ max}$ = 823, 1073 and 1273 K and coke with the particle size of 63～75 μm were reduced at T_R = 1173 K in N_2 gas atmosphere. The relationship between fractional reduction *F*(%) and reduction time at T_R = 1173 K is shown in Figure 10. Fractional reduction *F*(%) of the carbon composite pellet using semi-charcoal obtained at $T_{C,\ max}$ = 823 K was 40 % for 60 min and was also higher than any other pellets because of the difference volume of residual V.M., especially H_2. Moreover, fractional reduction *F*(%) of carbon composite pellets using semi-charcoals obtained at $T_{C,\ max}$ = 1073 K and 1273 K were much higher than the coke composite pellet. This result originates in the gasification rate. We confirmed that the gasification rates of semi-charcoal samples were higher than that of a coke sample. Therefore, all semi-charcoal composite pellets were reduced higher than the coke composite pellets. On the other hand, the carbon composite pellets using semi-charcoals obtained at $T_{C, max}$ = 1073 K with the particle sizes of 23～35, 63～75 and 105～150 μm were reduced at T_R = 1173 K in N_2 gas atmosphere in order to investigate the effect of semi-charcoal particle size. The relationship between fractional reduction *F*(%) and reduction time at T_R = 1173 K is shown in Figure 11. Fractional reduction *F*(%) of the carbon composite pellet using semi-charcoal with the particle size of 23～35 μm was 38 % for 60 min and was higher than any other pellets. When the size of semi-charcoal particle was smaller, the reduction rate of iron oxide was higher at T_R = 1173 K.

In consideration of these results, semi-charcoal composite pellets could be prepared and the effect of residual V.M. and gasification rate of semi-charcoal on reduction of iron oxide were clarified. Furthermore, the effect of the semi-charcoal particle size was also found. These results lead to the possibility of novel iron ore agglomerates.

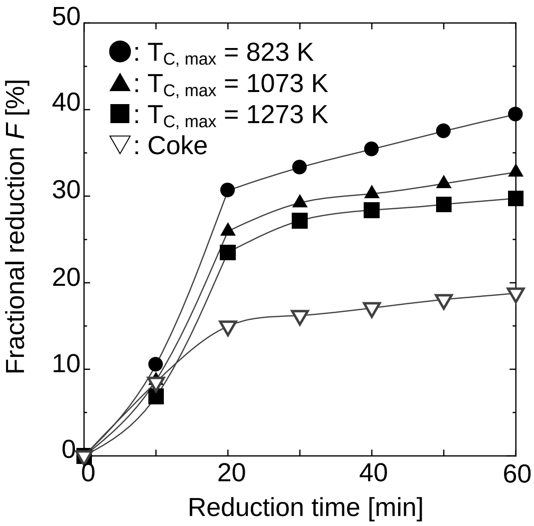

Figure 10. Reduction curves of carbon composite pellets using the semi-charcoal and coke with the particle size of 63～75 μm at T_R = 1173 K in N_2 gas atmosphere.

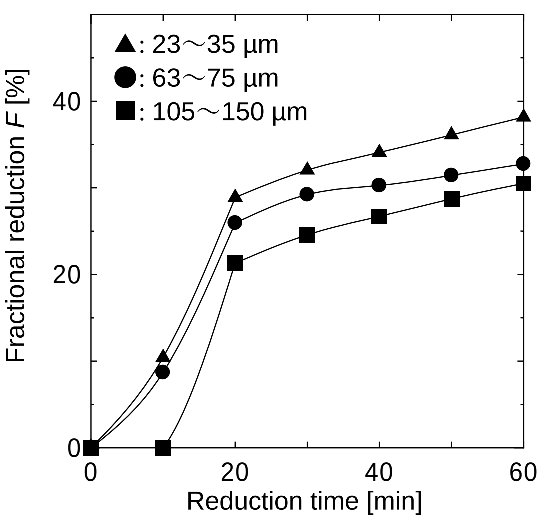

Figure 11. Reduction curves of semi-charcoal composite pellets at $T_{C, max}$ = 1073 K with the particle sizes of 23～63, 63～75 and 105～150 μm at T_R = 1173 K in N_2 gas atmosphere.

4 CONCLUSIONS

Carbon composite iron oxide pellets using semi-charcoal have been prepared and the reduction behavior were investigated. The results obtained are summarized as follows:

(1) The semi-charcoal obtained at $T_{C, max}$ = 823 K retained much V.M., mainly H_2.

(2) The gasification rate of a semi-charcoal sample obtained at $T_{C, max}$ = 823 K is the highest at all conditions, but the difference of rates in all semi-charcoal samples are much small. The activation energy was estimated as 138, 139, 162 and 219 kJ/mol, respectively for semi-charcoal obtained at $T_{C, max}$ = 823, 1073, 1273 K and coke samples.

(3) Fractional reduction *F*(%) of the carbon composite pellet using semi-charcoal obtained at $T_{C,\ max}$ = 823 K was over 40 % for 60 min and was also higher than any other pellets at T_R = 1173 K.

(4) Fractional reduction *F*(%) of the carbon composite pellet using semi-charcoal obtained at $T_{C,\ max}$ = 1073 K with the particle size of 23～35 μm was 38 % for 60 min at T_R = 1173 K and was higher than any other pellets. When the size of semi-charcoal particle was smaller, the reduction rate of iron oxide was higher at T_R = 1173 K.

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